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Effectiveness Testing of Spill-Treating Agents

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ABSTRACT

Laboratory effectiveness tests are described for four classes of spill-treating agents: solidifiers, demulsifying agents, surface-washing agents and dispersants. Many treating agents in these four categories have been tested for effectiveness and the results are presented here.

Solidifiers or gelling agents solidify oil, requiring a large amount of agent to solidify oil—ranging between 16% by weight, to over 200%. Emulsion breakers prevent or reverse the formation of water-in-oil emulsions. A newly-developed effectiveness test shows that only one product is highly effective: however, many products will work, but require large amounts of spill-treating agent.

Surfactant-containing materials are of two types, surface-washing agents and dispersants. Testing has shown that an agent that is a good dispersant is conversely a poor surface-washing agent, and vice versa. Tests of surface-washing agents show that only a few agents have effectiveness of 25–40%, where this effectiveness is the percentage of heavy oil removed from a test surface. Results using the 'swirling flask' test for dispersant effectiveness are reported. Heavy oils show effectiveness values of about 1%, medium crudes of about 10%, light crude oils of about 30% and very light oils of about 90%.

INTRODUCTION

Many oil-spill-treating agents have been promoted in the past 20 years. The total number of agents proposed world-wide is estimated to be 600.

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of which only about 100 were tested, even in a limited way (API, 1972). The high level of activity causes difficulties for the potential user and for the environmentalist because they are unable to discriminate between those products that will be beneficial and those that will not.

Effectiveness is the major difficulty with most treating agents. Effectiveness is generally a function of oil type and composition. Crude and refined oil products have a wide range of molecular sizes and composition including whole categories of materials like asphaltenes, alkanes, aromatics and resins. Agents that are effective for small asphaltene compounds in the oil may be ineffective on the large asphaltenes and agents that are effective on an aromatic compound may not be effective on a resin. To make matters worse, the composition of crude oils varies widely and this leaves little scope for a universally-applicable and effective spill-control chemical.

Testing of spill-treating agents in Environment Canada has involved [illegible] facets: the first is testing for aquatic toxicity and the second is effectiveness testing. The focus in this paper will be on laboratory effectiveness testing. Criteria for selection of laboratory test methods include: similarity to actual field test results and conditions; reproducibility of results; simplicity of apparatus and procedure; and correlation of results with those from other tests. Several projects have been initiated to develop tests and to complete testing of most currently-available spill-treating agents.

GELLING AGENTS OR SOLIDIFIERS

Gelling agents are those agents that change oil from liquid to solid. Also known as solidifiers, these agents often consist of polymerization catalysts and cross-linking agents. Agents which are actually sorbents are not considered to be gelling agents. Three solidifiers were tested by Environment Canada before the current round of experimentation:

1. The BP (British Petroleum) product which consists of deodorized kerosene and a cross-linking agent.
2. A Japanese product consisting of an amine which forms a polymer, and
3. The solidification agent proposed by Professor Bannister of the University of Lowell; an agent which uses liquefied carbon dioxide and an activating agent.

During tests conducted in the laboratory, all three agents functioned, but required large amounts of agent to solidify the oil effectively. Under some situations the oil becomes a viscous semi-solid; this transformation would not aid spill recovery. The BP agent worked better than the other agents and was tested on a larger scale by the Canadian Coast Guard and the Canadian oil industry. In these large-scale tests, large quantities of gelling agent were required to solidify the oil, in fact up to 40% of the oil volume which is double the laboratory requirement. Both requirements were deemed to be far in excess of what was practical during a real spill.

A standard test was developed to assess new solidifiers. The test consists of adding solidifier to a standard test oil under constant stirring until the oil is solid. The test results are repeatable within 5%. A summary of the test procedures is given in the Appendix and results of the current round of testing are presented in Table 1. Values are the weight percentage of the agent required to solidify an oil completely.

EMULSION BREAKERS

Several agents designated as emulsion breakers are largely hydrophilic surfactants; surfactants with a strong tendency to make oil-in-water emulsions. Such surfactants can reverse the water-in-oil emulsion to two separate phases. The problem with hydrophilic surfactants is that they are more soluble in water than in oil, and will quickly leave the oil. They cannot be successfully used on open water. Some recent products avoid this problem by using a less-water-soluble surfactant and accepting the resulting decrease in effectiveness. One recent product, 'Demoussifier', developed by Environment Canada, does not use surfactant in the normal sense of the word. This product does not suffer the limitations noted above.

Two commercial products, Exxon Breaxit and the Shell product, LA 1834, and a surfactant, sodium dioctyl sulfosuccinate were evaluated in

TABLE 1
Solidifier Test Results

Product name	*Percentage to solidify*
Rawflex	16
Norsorex	19
Oil Bond 100	33
Oil Sponge	36
Petro Lock	44
Molten wax	109
Powdered wax	278

one study (S. L. Ross Environmental Research, 1986). All three products funtioned in a limited way, but only the Shell product prevented the formation of emulsions over a wide range of oils and conditions. The Shell and Exxon products are not mass-produced, but can be obtained in small quantities for testing.

The Environment Canada product, Demoussifier, was tested in the laboratory in large tanks, and in a large-scale field trial. Results of the extensive testing on this product have been widely published (Fingas & Tennyson, 1988; Bobra *et al.*, 1988*a*, *b*; Seakem Oceanography, 1990).

A new laboratory test is under development at Environment Canada. The test is intended to provide a fast, convenient means of assessing emulsion preventers and breakers. A brief summary of the procedure is given in the Appendix and preliminary results of tests are given in Table 2. The minimum operative concentration is defined as the lowest concentration at which the emulsion volume is reduced to half its initial value. The percentage emulsion reduction is the percentage reduction in emulsion volume at a treating-agent concentration of 5000 ppm. The products tested included only one that was specifically intended for emulsion breaking, the others being dispersants or common household cleaners. Two products, Demoussifier and the dispersant Dasic Slickgone LTS, show good performance in these preliminary tests.

SURFACE-WASHING AGENTS

The most promoted and common treating agents are those containing surfactants as the major ingredient. These agents can be considered as falling into two categories: dispersants and surface-washing agents. Dispersants are those agents that have approximately the same solubility

TABLE 2
Preliminary Emulsion-Breaker Test Results

Agent	*Minimum operative concentration (ppm)*	*% Emulsion reduction at 5 000 ppm*
Demoussifier	<3 000	65
Dasic Slickgone	1 000	69
Palmolive	6 000	32
Enersperse 700	20 000	21
Corexit CRX-8	40 000	45
Corexit 9527	40 000	42
Mr Clean	Inoperative	1

in water and oil, and will cause the oil to be dispersed into the water in the form of fine droplets. Surface-washing agents are those agents that remove oil from solid surfaces such as beaches by a mechanism known as detergency. As it turns out, the mechanisms of dispersancy and detergency are quite different and testing has shown that a product that is a good surface-washing agent is a poor dispersant and vice versa.

A test for surface-washing agent effectiveness was developed by Environment Canada, and several commercial products have been tested using this protocol. The test measures how much oil is removed from a standard test surface after the surface-washing agent is allowed to soak into the oil, and after a water rinse. The Appendix contains a summary of the test procedure and Table 3 shows the results of these tests

TABLE 3
Surface-Washing Agent Test Results

Agent	*Oil removal (%)*	*Toxicity*	*Dispersant effectiveness (%)*
D-Limonene	52	35	0
Penmul R-740	44	24	9
Corexit 9580	42	>5 600	0
Formula 2067	39	11	0
Citrikleen XPC	36	34	2
Formula 861	32	24	0
Corexit 7664	27	850	2
BP 1100 WD	21	120	6
Re-Entry	17	8	0
Palmolive dish soap	16	13	9
Breaker 4	13	340	0
Nokomis 3	13	110	0
Citrikleen FC1160	12	75	0
Con-Lei	12	70	0
Sunlight dish soap	12	13	9
Citrikleen 1855	12	55	0
Bioversal	11	120	0
Mr Clean	6	30	0
Gran control	6	75	0
Corexit CRX-8	5	2	45
Formula 730	5	33	0
Corexit 9527	3	108	33
Tornado	3	1 350	0
Biosolve	2	9	0
Lestoil	1	51	0
Enersperse 700	1	50	51

with a seawater rinse and the results of an aquatic toxicity test (lethal concentration to half the test population of rainbow trout over four days in mg/litre: larger values suggest less toxicity) and a dispersant effectiveness test (swirling flask test, values represent percentage of oil put into the water column) for the same products. These latter data points were included to show the opposite nature of dispersant and surface-washing effectiveness. The point is highlighted in Fig. 1 where dispersant effectiveness is shown versus surface-washing effectiveness. This graph

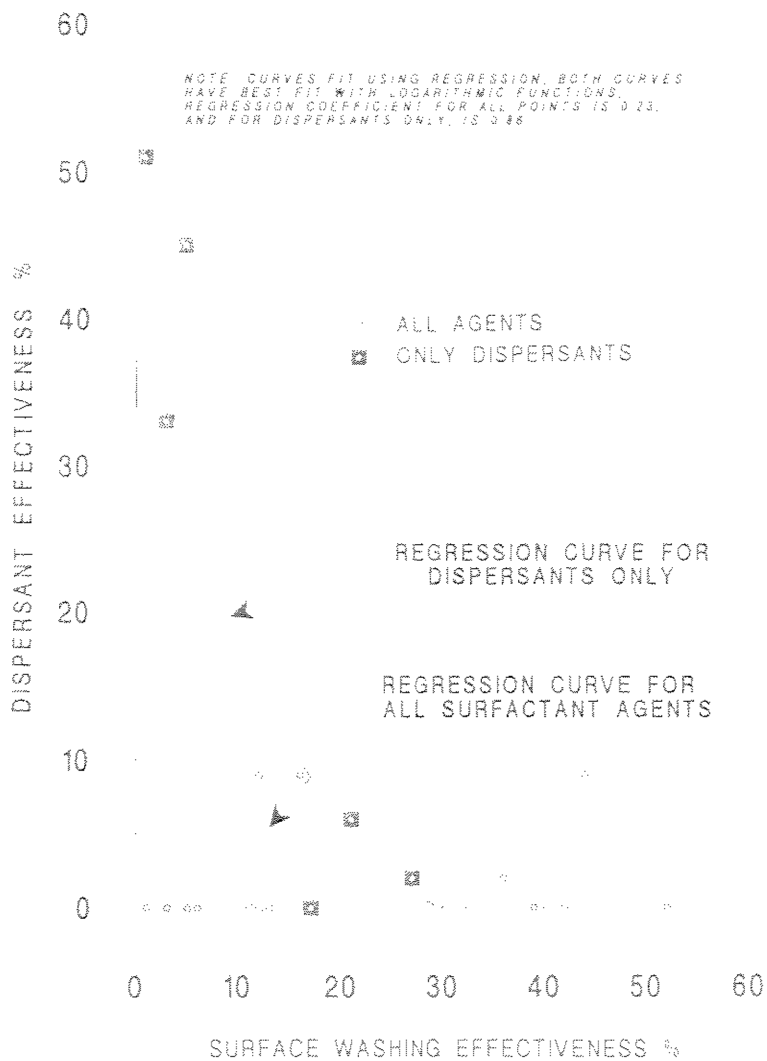

Fig. 1. Correlation of dispersant and surface-washing effectiveness.

shows that all surfactant agents show a strong tendency to be effective for only one function and this is especially evident in the curve where only traditional dispersants are included. Some products display neither property.

Low dispersant effectiveness is a benefit for any product that will be used as a surface-washing agent because oil can then be recovered rather than dispersed into the water column. Furthermore, because the two properties of detergency (surface-washing) and dispersancy are essential orthogonal, highly effective products do not have significant dispersant effectiveness.

The test oil for the surface-washing test is Bunker C and for the dispersant test is a light crude oil, Alberta Sweet Mixed Blend.

DISPERSANTS

Early dispersant effectiveness testing was largely tried in field situations. Over the past 12 years, 107 test spills have been laid out to test the effectiveness of oil-spill dispersants (Fingas, 1989). Most experimenters have not assigned effectiveness values because mass balances are nearly impossible to determine under field conditions. Of those that did, some experimenters simply estimated effectiveness from visual appearances but most based their measure on integrations of oil concentrations in the water column under the slick. It was presumed that the underwater plume had the same relative positions as the surface slick. This is not a correct means to perform the measurement because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different from surface dynamics (Brown & Goodman, 1988). Furthermore, all the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate and results in effectiveness values that are vastly exaggerated (Fingas, 1989). Surface measures are also inadequate at this time, but may be possible with the development of new remote sensors (Goodman & Fingas, 1988).

Several studies compared the test results from different laboratory apparatus and procedures. A review of these results shows that there is poor correlation in effectiveness results between the various test methods when these methods are followed as written (Fingas *et al.*, 1987). A recent study by the present author has shown that lack of correlation is primarily a function of oil-droplet settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus (Fingas *et al.*, 1989). Another important factor is the oil-to-water ratio used in the apparatus. When these two parameters are adjusted to be the same, and to larger values, test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests are higher but, when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Given that essentially identical results can now be obtained from almost any laboratory tests, a simple, repeatable and fast test can be chosen to make determinations of the dispersant effectiveness. One test developed by Environment Canada, called the 'swirling flask' test, meets these criteria and has been used to test many combinations of oils and dispersants as shown in Table 4. Test procedures are given in the Appendix.

A few trends are evident in these data. First, there is little difference between dispersants, other than the slight tendency of Dasic to disperse heavier oils better than the other dispersants, but lighter oils to a lesser degree. Secondly, the average effectiveness for heavy oils is about 1%, for

TABLE 4
Dispersant Effectiveness Results

	Effectiveness with dispersant (%)			
Oil	*Corexit 9527*	*Corexit CRX-8*	*Enersperse 700*	*Dasic*
Alberta	33	45	51	24
Arabian Light	17	9	22	33
Avalon	11	5	11	16
Bent Horn	17	20	23	30
Bunker C	1	2	2	1
California Heavy	1	1	1	1
Endicott	7	8	6	14
Endicott weathered	6	2	6	3
Hibernia	6	6	10	14
Hibernia weathered	4	3	8	7
Lago Medio	5	5	13	15
Norman Wells	36	43	51	26
Nuguini	50	57	55	28
Panuk	96	78	96	40
Prudhoe Bay	7	7	10	14
Prudhoe Bay weathered	4	4	8	10
South Louisiana	31	36	48	42
Synthetic crude	63	41	61	25
Transmountain	8	8	28	27
Used motor oil	33	31	36	29

medium crudes about 10%, for light crudes about 30%, and for very light oils about 90%. A light oil is defined here as one with a viscosity of 10–100 cSt at 15°C and includes such oils as Alberta. Very light oils are those which have a viscosity less than 10 cSt such as Panuk. Medium oils have a viscosity of 100–500 cSt such as Endicott, Hibernia and Prudhoe Bay. Heavy oils are those which have a viscosity greater than 500 cSt and include oils such as Bunker C and California Heavy. The final trend noted in the Table 4 data is that weathered oils are dispersed to a lesser degree than their fresh counterparts.

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APPENDIX—SUMMARY TEST PROCEDURES

1 Solidifier test

1.a Equipment
Stirrer—Labline model 134-2; stop watch; analytical balance.

1.b Supplies
Jar—1 litre wide-mouth jar; spatula—standard disposable; plastic spoon.

1.c Reagents
Crude oil—ASMB (Alberta Sweet Mixed Blend)—Environment Canada standard; salt water—deionized water with 33 ppt NaCl.

1.d Procedure
200 ml of seawater are placed into the jar and 20 ml of the standard oil is weighed and placed on the water. The temperature of the water and oil are maintained at 20 °C. A stirrer is placed at the oil–water interface and turned on. After one min, quantities of the solidification agent are added at 1-min intervals from a pre-weighed container. A plastic spatula is used to test the solidity of the oil. When the oil is solid by appearance, the weight of solidifier added, and weight of the oil, are used to calculate the percentage required to solidify. Repeatability is 12% of the absolute value of the minimum operative concentration.

2 Emulsion breaker test

2.a Equipment
Wrist-action Burrell model 75; Vernier callipers; stop watch.

2.b Supplies
500 ml graduated cylinder; pipette with 1 ml capacity.

2.c Reagents

Salt water – deionized water with 33 ppt NaCl; test oil known to form emulsions—a mixture of half (by volume) Bunker C with half ASMB (Alberta Sweet Mixed Blend), weathered until a volume loss of 20% is achieved.

2.d Procedure

Place 400 ml water in the cylinder and 1 ml oil on the surface of this water. Place the oil in the shaker and shake through an angle of 2° for a period of 40 min. Stop the shaker and measure the height of the emulsion with the callipers both along the shaking axis and perpendicular to it. The height of the emulsion is taken as the average of these two numbers. The treating agent is added and the cylinder shaken for another 60 min. The height of the emulsion is taken again and used to calculate the percentage reduction for that quantity of treating agent. The minimum quantity is taken as the concentration of agent that causes a 50% reduction in emulsion height.

3 Surface-washing agent test

3.a Equipment

Analytical balance; stainless steel trough ($\frac{1}{4}$ in angle stock—20 cm long).

3.b Supplies

Positive-displacement pipettes—capacity 150 μl and 30 μl; 50 ml syringe with 18 gauge needle; tissue; tweezers.

3.c Reagents

Salt water—deionized water with 33 ppt NaCl.

3.d Procedure

The temperature of the reagents and apparatus is maintained at 20 °C. Place 0·15 ml of the test oil onto a 50 mm strip in the centre of the trough. Let the oil stand for 10 min and then weigh the oil and trough. Apply 0·03 ml of the surface-washing agent to the oil and distribute it along the test oil strip. Let the material soak for 10 min. Place the trough in a stand at 15° from horizontal and, using the 50 ml syringe with an 18 gauge needle as a funnel, flush the surface with 5 ml water. Let stand for another 10 min and flush again with the same amount of water. Let dry for 10 min and carefully remove any remaining water droplets with tweezers and a tissue. Weigh the trough to determine the weight of oil removed. Repeatability of the test results are within 6%.

4 Dispersant test (swirling flask procedure)

4.a Equipment

Laboratory shaker—New Brunswick Scientific Gyrotary Shaker Model G2 or model G-27; visible spectrometer.

4.b Supplies

125 ml Erlenmeyer flask with bottom spout; positive-displacement pipettes—capacity 100 μl, 10 μl and 5 μl; 250 ml separatory funnels; graduated cylinders—capacity 30 ml and 5 ml.

4.c Reagents

Test oil; spectrophotometric grade methylene chloride; salt water—deionized water with 33 ppt NaCl.

4.d Procedure

Dispersant is pre-mixed with the oil at a ratio of 1 : 25 (dispersant : oil). Place 120 ml of water into the test flask and float 0·1 ml oil/dispersant on the water. The temperature of the water and oil is maintained at 20°C. Shake the flask(s) for 20 min at 150 rpm. Let stand for a further 10 min and take a 30 ml sample through the side-spout. Extract the oil with 3 successive aliquots of 5 ml of dichloromethane. Read the absorbency of the combined dichloromethane extracts in a spectrophotometer at 340, 370 and 400 nm. Using a calibration curve, determine the percentage effectiveness at each wavelength and average for the final result. Effectiveness results are repeatable within 12% at high effectiveness values (30–100%) and within 5% at low values (<30%).

Calibration curves are prepared by adding the amount of oil calculated to yield a given percentage to 30 ml water and proceeding as though this is a regular run.